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END OF YEAR REPORT FOR 1 OCTOBER 1984 THROUGH 30  
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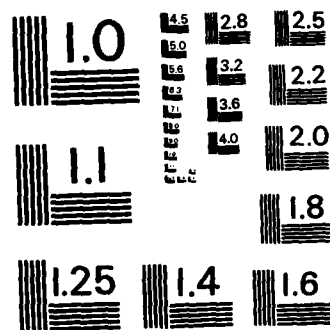
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OFFICE OF NAVAL RESEARCH

END OF YEAR REPORT

for

1 October 1984 through 30 September 1985

for

Contract No. H84K0289

N00014-84-K-0289

NR-627-841

C. A. Angell

Purdue University  
Department of Chemistry  
West Lafayette, Indiana 47907

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Part I

a. Papers Submitted to Refereed Journals (and not yet published)

1. Changle Liu and C. A. Angell, Mechanical vs Electrical Relaxation in AgI-based Fast Ion Conducting Glasses, J. Non. Cryst. Solids 1986 (in press).
2. E. I. Cooper and C. A. Angell, Ambient Temperature Plastic Crystal Fast Ion Conductors (PLICFICS), Solid State Ionics 1986 (in press).
3. Changle Liu, H.G.K. Sundar, and C. A. Angell, All-Halide Superionic Glasses, Solid State Ionics 1985 (in press).
4. Changle Liu and C. A. Angell, Mechanical Relaxation by Mobile Ions Cu<sup>+</sup> and Ag<sup>+</sup> in Fast Ion Conducting Glasses, J. de Physique 1985 (in press).
5. C. A. Angell, Recent Developements in Fast Ion Transport in Glassy and Amorphous Materials, (text of plenary lecture) Solid State Ionics.

b. Papers Published in Refereed Journals.

1. C. Liu, H.G.K. Sundar, and C. A. Angell, Silver Alkali Halide Glasses and a Vitreous Analog of the RbAg<sub>4</sub>I<sub>5</sub> Superionic Conductor, Mat. Res. Bull. 20 (1985) p 525.

c. Books: None.

d. Books published: None.

e. Patents filed: None.

f. Patents granted: None.

g. Invited Presentations at Topical of Scientific/Technical Conferences

1. Fast Ion Phenomenology in Glassy Solids, Transport in Solids, Symposium American Chemical Society National Meeting, Miami Florida, May 2, 1985.
2. "Fast Ion Phenomenology in Glassy Solids", Great Lakes Regional American Chemical Society, Symposium on Solid State Chemistry, Purdue University, West Lafayette, Indiana, June 11, 1985.
3. Recent developements in Fast Ion Transport in Glassy and Amorphous Materials, Plenary lecture, 6th International Congress on Solid State Ionics Lake Tahoe, California, August 21, 1985.

h. Contributed Presentations at Topical or Scientific/Technical Society Conferences

1. "Mechanical Relaxation by Mobile Ions Cu<sup>+</sup> and Ag<sup>+</sup> in Fast Ion Conducting Glasses" presented at the 3rd International Conference on Ultrasonic and Internal Friction, Urbana, Illinois, June 1985, by Changle Liu.

2. Ambient Temperature Plastic Crystal Fast Ion Conductors (PLICFICS) presented at the 5th International Congress on Solid State Ionics at Lake Tahoe by E. I. Cooper.

3. "All-Halide Superionic Conducting Glasses" presented at the 5th International Congress on Solid State Ionics at Lake Tahoe by E. I. Cooper.

i. Honors/Awards/Prizes: invited Plenary lecture at 5th International Congress on Solid State Ionics, see (g.) above.

## Part II

a. Funding under the present contract was commenced in 1983 at the level of \$55,000.00. This was increased to the current \$72,000.00 for the year 1984-1985. The contract has been reviewed for a third year at the same level.

b. Current telephone number: (317)494-5256.

c. The project involves a range of measurements aimed at elucidating the properties of fast ion conducting glasses by electrical conductivity and mechanical relaxation studies in addition to normal characterization measurements. Work on Plastic Crystal Fast Ion Conductors was included in the early part of the 1983-1984 fund year but transferred to other agency support during that period. The overall objective of the work is to explore the potential of glass forming systems which provide new and potentially useful solid electrolyte systems. The systems are being characterized by a combination of normal impedance studies and mechanical relaxation measurements using a dynamical mechanical analyzer. Both lithium and silver/copper-containing glasses are being investigated, most effort so far has gone into the development and characterization of unusual  $\text{Ag}^+$  and  $\text{Cu}^+$  containing systems.

d. Significant results during the last year:

1. Copper ( $\text{Cu}^+$ ) analogs of the new All-halide glasses (described by us for  $\text{Ag}^+$  glasses recently) have been prepared and characterized (see Part I a 3).

2.  $\text{CuI-CuPO}_3$  glasses have been studied by both mechanical and electrical relaxation spectroscopy (see Part I a 4).

3. Most recently, some very interesting crystallization phenomenology and mixed anion effects are being observed in  $\text{AgI-Ag}_2\text{SO}_4\text{-Ag}_2\text{WO}_4$  systems. The effects of replacing small amounts of  $\text{SO}_4^{2-}$  with the larger tungstate anion, are extraordinary. An attempt to do spectroscopic relaxation studies failed for technical reasons.

e. Plans for coming year:

We will continue the study of nucleation kinetics in the unusual system referred to above since it seems to behave so anomalously yet so reproducibly. We will also pursue to mixed anion effect by mechanical and electrical relaxation studies to see how effectively the conductivity can be enhanced, and to understand the mechanism. We will compare exchange of  $\text{SO}_4^{2-}$  with  $\text{WO}_4^{2-}$ , with exchange of  $\text{I}^-$  with  $\text{Br}^-$ . If possible we will introduce the pressure variable into these studies, partly

to check claims that conductivity can be increased by pressure on the glass, and partly to see for the first time the effect on glass conductivity of pressure applied to the liquid before glass formation (in which case the glass structure is changed). Finally we will tackle the one part of our originally proposed work not yet dealt with viz., the replacement of O with S in  $WO_4^{=}$  and  $W_2O_7^{=}$  containing glasses.

f. Currently on project:

Graduate students: Hemlata Senapati (visiting)

Post doctoral fellows: Changle Liu (departing) Rongjian Xue

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OFFICE OF NAVAL RESEARCH  
Contract No. N00014-84-K0289  
TECHNICAL REPORT, SEPTEMBER 1985  
Report No. 2

MECHANICAL RELAXATION BY MOBILE IONS ( $\text{Cu}^+$  AND  $\text{Ag}^+$ )  
IN FAST ION CONDUCTING GLASSES

C. A. Angell  
Prepared for publication in  
J. de Physique

Purdue University  
Department of Chemistry  
West Lafayette, IN 47907

September 1985

Prepared for  
Office of Naval Research  
800 N. Quincy Street  
Arlington, VA 22217  
Division of Sponsored Programs  
Purdue Research Foundation  
Purdue University  
West Lafayette, IN 47907

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
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		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Changle Liu and C. A. Angell		8. CONTRACT OR GRANT NUMBER(s) N00014-84-k0289
9. PERFORMING ORGANIZATION NAME AND ADDRESS Purdue University Department of Chemistry West Lafayette, IN 47907		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The dissipation of mechanical energy in glasses of the "fast ion conductor" type ( $\text{AgI-AgPO}_3$ ), $\text{AgI-AgBO}_2$ , and $\text{AgCl-CsI}$ ) has been studied using a Rheovibron mechanical analyzer in the temperature range $-190$ to $200^\circ\text{C}$ . In most cases a single loss peak at low temperature is found for fixed-frequency scans. The peak temperature almost coincides with that for electrical conductivity relaxation but is much broader. The loss magnitude does not correlate with peak temperature but depends on glass constitution. Where loss is small, the relaxation time follows Arrhenius Law with $\tau_0 = 1/2\pi f_0$ is found from far IR spectra.		

For large loss glasses, important non-Arrhenius behavior is found.

# MECHANICAL RELAXATION BY MOBILE IONS ( $\text{Cu}^+$ AND $\text{Ag}^+$ ) IN FAST ION CONDUCTING GLASSES

Changle Liu and C. A. Angell  
Department of Chemistry  
Purdue University  
West Lafayette, Indiana 47907, U.S.A

## Résumé

**Abstract** - The dissipation of mechanical energy in glasses of the "fast ion conductor" type ( $\text{AgI-AgPO}_3$ ,  $\text{AgI-AgBO}_2$  and  $\text{AgCl-CsI}$ ) has been studied using a Rheovibron mechanical analyzer in the temperature range  $-190$  to  $200^\circ\text{C}$ . In most cases a single loss peak at low temperature is found for fixed-frequency scans. The peak temperature almost coincides with that for electrical conductivity relaxation but is much broader. The loss magnitude does not correlate with peak temperature but depends on glass constitution. Where loss is small, the relaxation time follows Arrhenius Law with  $\tau_0 = 1/2\pi f_0$ , where  $f_0$  is found from far IR spectra. For large loss glasses, important non-Arrhenius behavior is found.

## INTRODUCTION

Although the technological need for solid electrolytes has led to an explosive increase in the number of conductivity studies in crystalline and vitreous ionic materials, there has been relatively little attention given to the response of the mobile ions to mechanical, as opposed to electrical, stresses. Apart from classic studies focussed on normal oxide glasses, there has only been the ultrasonics study of Carini and colleagues on  $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$  glasses [1]. This is unfortunate because the mechanical response is qualitatively different from the electrical response insofar as the real part of the modulus remains finite at low frequencies. An electrical stress acting on the same ions will be completely dissipated by the unimpeded motion of the ions across the sample. Furthermore, the mechanical response is a secondary relaxation, the primary relaxation being that which leads to the glass transition.

For the classical (weakly-conducting) glasses, the investigation of mobile ion motion is tedious because of the small magnitude of the loss. For fast ion conductors, on the other hand, the losses are much greater, and less-sensitive instruments such as a Rheovibron (Toyo Instruments Inc.) may be employed with a resultant increase in rate of data acquisition of at least one order of magnitude.

In this report we describe essential features of the mechanical response of three types of fast ion conductors over wide temperature ranges.

## EXPERIMENTAL SECTION

The principles of the measurement are illustrated in Fig. 1. Two sample configurations are in common use. The first utilizes a fiber which is held between stainless steel jaws connected to the frequency generating and stress/strain detecting elements of the Rheovibron. A sinusoidal strain  $\alpha_1$  is applied, and the lag of the stress  $\alpha_2$  behind the strain is recorded as the loss tangent illustrated in the lower part of the figure. The second, from which the same information can be acquired, uses the

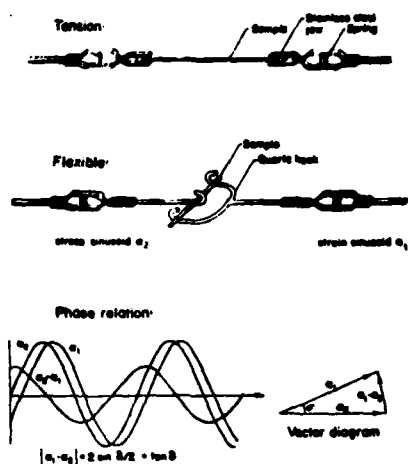


Fig. 1 - Principles of measurement.

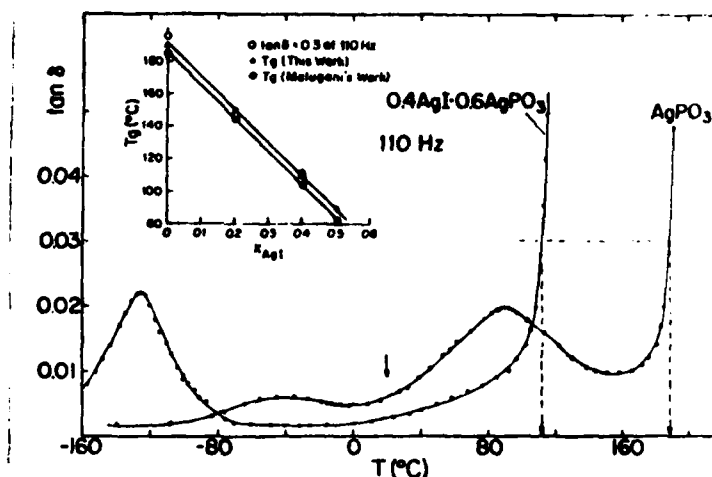


Fig. 2 - Loss scans for AgI-AgPO<sub>3</sub> glasses.

flexure configuration illustrated in the center section of Fig. 1. The jaw/sample assembly is enclosed in a variable temperature metal block, and the loss tangent and dynamic modulus at constant frequency are read at frequent intervals during a slow temperature scan from -200 to +200°C (as needed).

## RESULTS

Complete scans, from the low temperature regime where the "mobile ion" loss is recorded, up to the high temperature limit where the viscoelastic relaxation occurs (large loss with sample stretching) is illustrated in Fig. 2. Two compositions in the system AgPO<sub>3</sub>-AgI are represented. The agreement of the viscoelastic loss temperature with the usual (DSC) glass temperature T<sub>g</sub>, is shown in the insert. Details of the low temperature peak of interest to this work are shown in Fig. 3. Some data for the system Cu<sub>2</sub>O·P<sub>2</sub>O<sub>5</sub>-Cu(I or Cl) are shown in Fig. 4.

The storage and loss data are combined to give the real and imaginary parts of the tensile modulus, E' and E'' respectively, in Fig. 5. Results are shown for two frequencies, although the frequency dependence of the response is only clearly seen in the imaginary part.

Comparison with electrical responses is made in Fig. 6 for a composition in the AgI-AgPO<sub>3</sub> system using an inverse temperature scale to cast the data in a form similar to that obtained for frequency scans at constant temperature. The latter are shown, in the insert, for the electrical modulus, M'' (M'' = 1/ε\*). Fig. 6 brings out the important fact that, while both responses show maxima in their loss curves at

Fig. 3 - Loss "spectra" due to mobile ions in AgI-PO<sub>3</sub> glasses.

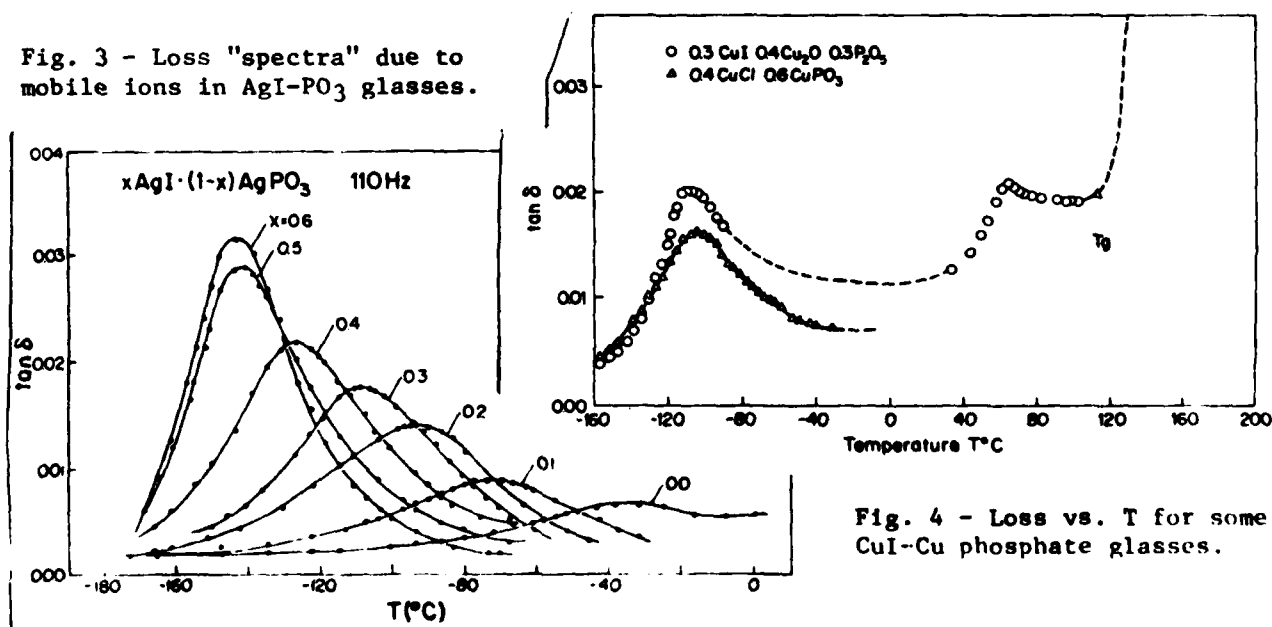


Fig. 4 - Loss vs. T for some CuI-Cu phosphate glasses.

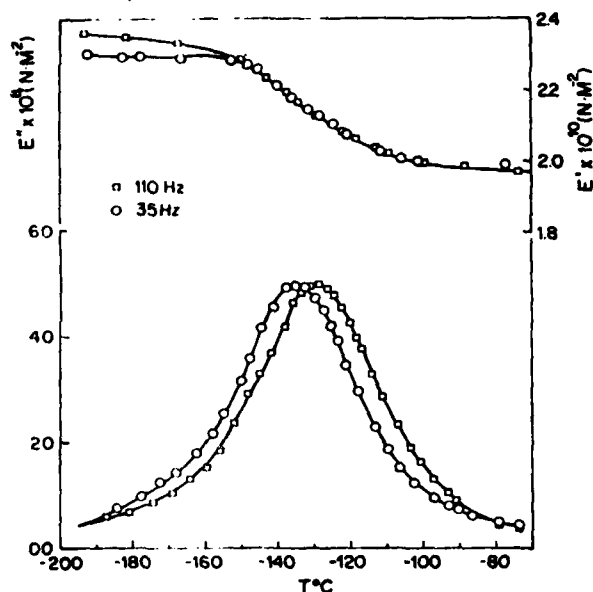


Fig. 5 - Real and imaginary parts of the complex tensile modulus.  $E'$  is discrepant for 35 Hz. Sample:  $(\text{AgI})_{0.6}(\text{Ag}_2\text{O} \cdot 0.2\text{B}_2\text{O}_3)_{0.4}$ .

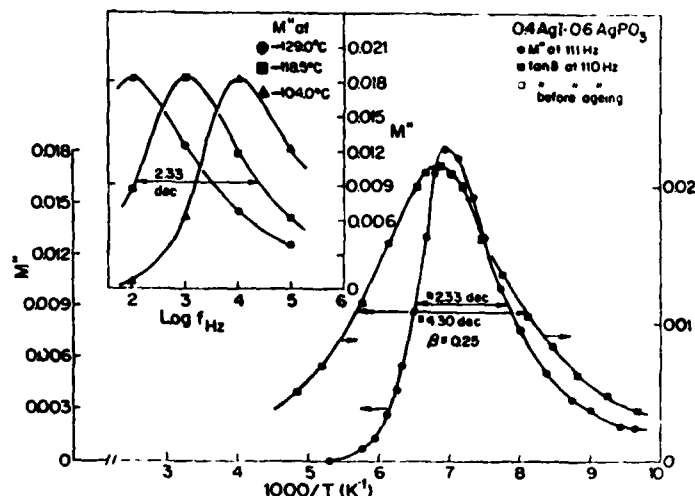


Fig. 6 - Comparison of electrical and mechanical loss moduli plotted vs.  $1/T$  to give same shape as isothermal spectra shown in insert.

approximately the same temperature (i.e. the most probable relaxation time is not very different) the mechanical response is much broader, particularly on the high temperature (low frequency) side. Indeed, there are temperatures at which the electrical loss has almost vanished while the mechanical loss is still half its maximum value. The electrical relaxation is described by  $\theta(t) = \exp - [(t/\tau)^\beta]$  with  $\beta = 0.46$ .

A comparison of loss peaks amongst systems of different constitution, including the recently developed all-halide glasses of the type  $\text{AgI-AgCl-CsCl}$ , is made in Fig. 7. This figure brings out the important point that systems of comparable relaxation time may have very different loss magnitudes (implying that different fractional modulus changes are not correlated with the ionic mobility).

#### DISCUSSION

The outstanding features of the present findings are (1) the magnitude of the loss in some but not all cases compared to previous glass studies, (2) the fact that most probable times for electrical and mechanical relaxation are closely similar while the spectral widths are very different and (3) the fact that despite the different widths (which could be taken to indicate different activation energy distributions /1/) the activation energies for the two types of relaxation are indistinguishable. We discuss these in turn.

Data for a single system, e.g.  $\text{AgI-AgPO}_3$ , Fig. 3, would suggest that the loss, which is proportional to the fractional change in modulus due to relaxation, scales with the log of the relaxation time. However, the new data for the all-halide system show this is not so. Thus, attention must be redirected from the mobility of the silver ions towards the nature of the matrix within which they move. We note there are no asymmetric anions in the case of the halide glass while there are triangular ( $\text{BO}_3$ ) groups in the very lossy borate compared with tetrahedral ( $\text{PO}_4$ ) groups in the phosphate glass.

In considering the meaning of the much greater spectral width for mechanical compared with electrical relaxation we note again the qualitative difference between the two responses. Given time, the electrical response completely relaxes an applied stress, i.e. there is no zero-frequency electrical modulus. By contrast, the mechanical response relaxes the modulus to a zero-frequency value just 5-15% less than the high frequency value. Furthermore, the mechanical relaxation, unlike the electrical, is secondary in nature, the primary relaxation having been that which is observed at the glass transition. The electrical relaxation is well described by the Fourier transform of the Kohlrausch-Williams-Watts (KWW) relation  $\theta(t) = \exp - [(t/\tau)^\beta]$ , with  $\beta$

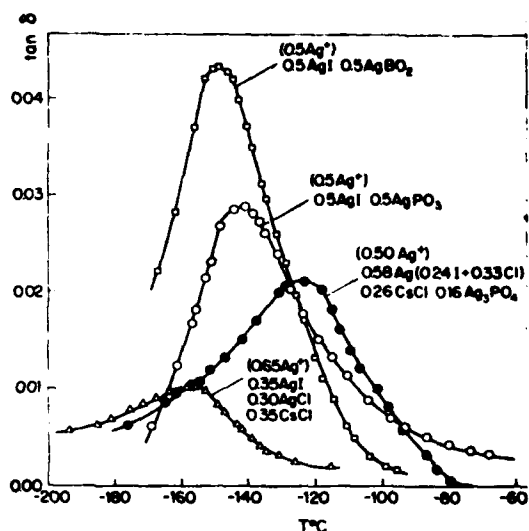


Fig. 7 - Comparison of loss peaks for different glasses.

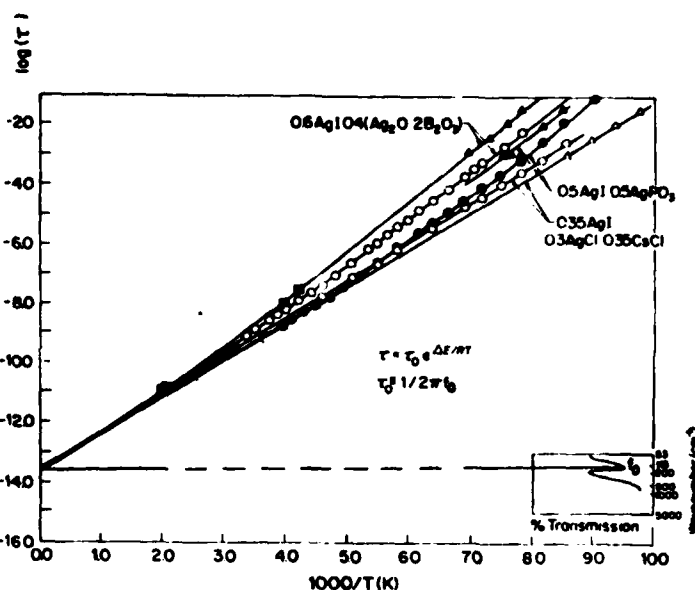


Fig. 8 - Electrical and mechanical relaxation times and relation to IR spectrum.

in the range 0.45-0.50 for all cases. The adequacy of the KWW form for the mechanical spectra has not yet been properly evaluated due to lack of sufficient measuring frequency range and precision. However, should this form be appropriate, then the peak halfwidths imply  $\beta$  values as small as 0.2 which will have to be rationalized by theory. Comparable widths in  $1/T$  have been found in the ultrasonic range /1/, though, by GHz frequencies, a remarkable narrowing to give single relaxation time behavior has very recently been observed /2/.

Finally, we examine the temperature dependence of the relaxation process. The relaxation times  $1/2\pi f$  are plotted vs. the  $1/T$  values at which the loss maxima are found, in Fig. 8, for all the  $\text{Ag}^+$  systems discussed in this paper. Fig. 8 shows that the least lossy glass exhibits Arrhenius behavior for both conductivity and mechanical relaxations with a simple extrapolation to the  $\text{Ag}^+$  quasi-lattice "rattling" time ( $1/2\pi f_0$ ) observable in the far IR (Fig. 8 insert). The more lossy glasses show regions of non-Arrhenius behavior. For the borate glass, extended-range mechanical relaxation studies /1,2/ permit characterization down to  $\tau = 10^{-4}$  sec, see Fig. 8. These data support extrapolations of the nonlinear Arrhenius plots to the same far IR frequency. These results are analyzed in more detail elsewhere /3/.

#### ACKNOWLEDGMENTS

Supported by ONR Grant No. N84k0289 and NSF-MRL Grant No. DMR 8316988.

#### REFERENCES

- /1/ (a) Carini, G., Cutroni, M., Federico, M. and Galli, G., Solid State Comm. 44 (1982) 1427.  
 (b) Carini, G., Cutroni, M., Federico, M., Galli, G. and Tripodo, G., J. Non-Cryst. Solids 56 (1983) 393.
- /2/ Borgesson, L., Martin, S. W., Torell, L. M. and Angell, C. A., Phys. Rev. Lett. (submitted).
- /3/ Liu, Changle and Angell, C. A., J. Non-Cryst. Solids (submitted).

OFFICE OF NAVAL RESEARCH  
Contract No. N00014-84-K0289  
TECHNICAL REPORT, SEPTEMBER 1985  
Report No. 3

AMBIENT TEMPERATURE PLASTIC CRYSTAL  
FAST ION CONDUCTORS (PLICFICS)

C. A. Angell  
Prepared for publication in  
Solid State Ionics

Purdue University  
Department of Chemistry  
West Lafayette, IN 47907

September 1985

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Polymer-salt type solid electrolytes are currently in favor because the electrolyte can change shape under mechanical stress without failure. A disadvantage, however, is that anion transport numbers are not zero. We think the former advantage can be had without the latter disadvantage by using an appropriate anion rotator phase in which the cation, or one of the cations, is mobile. $\text{Li}_2\text{SO}_4$ is the prototype material of this type but is limited to high temperature applications. We describe a low temperature material - a double salt of $\text{LiBF}_4$ and methoxyethyl dimethyl ethyl ammonium		

fluoroborate - which may conduct by the same mechanism as  $\text{Li}_2\text{SO}_4$  since it exhibits a strong disordering transition at  $-90^\circ\text{C}$ , and a relatively small entropy of fusion. At  $75^\circ\text{C}$  this substance conducts almost as well as the best polyethylene oxide + Li salt combination reported to date. Some variants on the structural theme and their properties and performance will also be described.

## AMBIENT TEMPERATURE PLASTIC CRYSTAL FAST ION CONDUCTORS (PLICFICS)

E. I. Coopers\* and C. A. Angell  
Department of Chemistry  
Purdue University  
West Lafayette, IN 47907

Polymer-salt type solid electrolytes are currently in favor because the electrolyte can change shape under mechanical stress without failure. A disadvantage, however, is that anion transport numbers are not zero. We think the former advantage can be had without the latter disadvantage by using an appropriate anion rotator phase in which the cation, or one of the cations, is mobile.  $\text{Li}_2\text{SO}_4$  is the prototype material of this type but is limited to high temperature applications. We describe a low temperature material - a double salt of  $\text{LiBF}_4$  and methoxyethyldimethyl ethyl ammonium - fluoroborate - which may conduct by the same mechanism as  $\text{Li}_2\text{SO}_4$  since it exhibits a strong disordering transition at  $-90^\circ\text{C}$ , and a relatively small entropy of fusion. At  $75^\circ\text{C}$  this substance conducts almost as well as the best polyethylene oxide + Li salt combination reported to date. Some variants on the structural theme and their properties and performance will also be described.

### INTRODUCTION

A requirement of the electrolyte in a solid state battery, which is as important as its d.c. conductivity, is its ability to adhere to and maintain good ohmic contact with the electrode materials. It is primarily this property which has led to the choice of polymer solvent + salt solutions for developmental solid state battery systems,<sup>1,2</sup> despite their rather poor ambient temperature conductances.<sup>3</sup>

Polymeric materials can distort easily and recoverably because of the existence of many liquid-like degrees of freedom which allow their constituent particles to rearrange locally under deforming stresses. Larger scale plastic flow is inhibited by polymer chain entanglements. Another type of solid which is characterized by the existence of many liquid-like degrees of freedom is the plastic crystal. In these, the presence

of relatively free rotation are of a fraction of the constituent particles, gives both a low elastic modulus and an ability to distort by local plastic flow involving molecular diffusion. It is therefore natural that effort be expended to find plastic crystalline materials in which ions of electrochemical interest such as  $\text{Li}^+$  are rapidly diffusing. Such materials merit the acronym PLICFIC (Plastic Crystalline Fast Ionic Conductor).

One of the most impressive of the known PLICFICs is  $\text{Li}_2\text{SO}_4$  in which the conductivity in the region immediately below the fusion point is of order  $1 \text{ ohm}^{-1} \text{ cm}^{-1}$  and in which fusion is actually accompanied by a decrease in conductivity. This compound, extensively studied by the Chalmers group<sup>4-6</sup> and recently examined in molecular detail by molecular dynamics methods,<sup>7</sup> is thought to conduct via a coupled anion rotation-cation diffusion ("paddle wheel" or "revolving door") mechanism.<sup>4-6</sup> The material is remarkable for the number of liquid-like degrees of freedom which it

\*Present address: IBM, T. J. Watson Research Center,  
P.O. Box 218, Yorktown Heights, NY 10598.

manifests, the center-of-mass order of the anion sublattice being the only crystalline structural characteristic which it retains.

The  $\text{Li}_2\text{SO}_4$  FIC phase unfortunately becomes unstable below  $500^\circ\text{C}$ , and in any case, its conductivity extrapolated to the interesting temperature range  $0-100^\circ\text{C}$  is not of special interest ( $\sim 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ ). Clearly what is desirable is a low temperature analogue of this type of material.

The appropriate route to such a material evidently will involve a reduction in the cohesive forces, hence a reduction in the anion charge. Indeed, considerable effort has been expended in the study of compounds such as  $\text{LiMCl}_4$ <sup>8,9</sup> with this aim in mind. Phases with rotationally excited states of the tetrahedral anion appear to exist in  $\text{LiAlCl}_4$  and  $\text{LiFeCl}_4$  near the respective fusion points but are unstable at lower temperatures.

Further reductions in cohesive forces may be expected if large organic cations are introduced into the structure. An attractive possibility in such compounds is that plasticity may be enhanced by temperature-induced rotational disorder of quasi-ellipsoidal organic cations. We have described elsewhere<sup>10</sup> several tetraalkylammonium salts which exhibit the thermodynamic characteristics of plastic crystals. We have also found that Li salts frequently form 1:1 compounds with tetraalkylammonium salts. We were therefore quite prepared to find our first low-temperature "PLICFIC" among these compounds, although its discovery was somewhat accidental. While investigating the conductivity of a supercooled liquid in the system  $\text{LiBF}_4 + \text{CH}_3\text{OCH}_2\text{CH}_2\text{N}^+\text{Me}_2\text{EtBF}_4^-$ , the sample froze unnoticed and the conductivity measured was found surprisingly to be only slightly lower than that of the liquid. Our attention naturally turned to the 1:1 compound in this system, which was the main phase in the frozen mixture. In this paper we describe this compound (and a few others closely related to it) and express the hope that it may be the forerunner of a family of such materials, some of which may have use-

ful applications in solid state electrochemical devices.

## EXPERIMENTAL SECTION

### Materials

$\text{LiBF}_4$  was obtained 98% pure from Alfa Inorganics. Since water was the main impurity it was dried in vacuo at  $100^\circ$ , under a  $\text{BF}_3$  partial pressure slightly exceeding its own, which was supplied by a "sacrificial" portion of  $\text{LiBF}_4$  (previously dried with slight decomposition) held at ca.  $130^\circ$ .

The various quaternary ammonium salts detailed below (Table 1) were prepared in 2 or 3 steps, following largely standard procedures:

- Conversion of the commercially available chloroethyl methyl ether (or chloroalkane) into the iodide by refluxing with NaI in acetone.
- Reaction of the organic iodide (or of the original organic chloride) with a tertiary amine ( $\text{NMe}_3$ ,  $\text{NMe}_2\text{Et}$ ), in acetonitrile, in a pressure bottle (or, when the chloride was chloromethyl methyl ether - in dry ether, with cooling), to form the quaternary ammonium halide. This was subsequently recrystallized from acetonitrile, ethanol or acetone by addition of anhydrous tetrahydrofuran or ether.
- Preparation of the quaternary ammonium tetrafluoroborate by addition of a stoichiometric amount of  $\text{AgBF}_4$  (Ozark-Mahoning, 99%) as its 10% solution in acetone to a solution of the halide in acetonitrile or acetone. If solid at  $T < 50^\circ\text{C}$ , the product was recrystallized from acetone or dichloromethane by addition of tetrahydrofuran or chloroform. Liquid salts were redissolved several times in dry tetrahydrofuran which was then evaporated in vacuo by rotary evaporator. Repeated extractions with chloroform were found helpful in the removal of most remaining halide from the liquid and lower-melting salts. A similar procedure, lead perchlorate in aqueous acetone replacing the silver salt, was followed to obtain the perchlorate (3 in Table 1).

Purity of the products was checked by elemental analysis; in several cases the virtual absence of water

was ascertained by Karl-Fischer titration. (The elemental analysis of compounds 7, 12 and 14 in Table 1 must be considered less than satisfactory, but DSC runs leave no doubt as to the distinct character of the compounds.) The tetrafluoroborate salts had the melting points included in Table 1.

To obtain the double salts with lithium tetrafluoroborate, perchlorate, or iodide, weighed quantities of the components were fused in a dry box at 120-150°C. The melting points of the double salts

are included in Table 1. Attempts were also made to prepare tetrachloroaluminates and tetrachlorogallate double salts of the same type (see Discussion).

#### Thermal characterization.

The various phase transitions and melting points of the substances under study were determined using ~10 mg samples contained in sealed aluminum pans using the Perkin-Elmer DSC-4 differential scanning calorimeter. All runs were conducted at 20° min<sup>-1</sup>

Table 1. Phase transitions of tetraalkylammonium salts and their lithium salt complexes.

No.	Compound	T <sub>g</sub> <sup>a,b</sup> /°C	T <sub>tr</sub> /°C(ΔH <sub>tr</sub> ) <sup>c</sup>	T <sub>m</sub> (ΔH <sub>m</sub> ) <sup>c</sup>
1	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> BF <sub>4</sub> <sup>-</sup>	-98	-	13(21.7)
2	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> BF <sub>4</sub> <sup>-</sup> ·LiBF <sub>4</sub>	-79	-79(3.9);62(1.7)	98(5.6)
3	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> ClO <sub>4</sub>	-90	-	2(14.7)
4	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> ClO <sub>4</sub> ·LiClO <sub>4</sub>	-	26(0.8);40(1.2) <sup>d</sup>	124(6.6)
5	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> I <sup>-</sup>	-52	-	47
6	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> I <sup>-</sup> ·LiI	-6	-	104(4.4)
7	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> Me <sub>3</sub> BF <sub>4</sub> <sup>-</sup>	-	-53(0.5)	64(20.9)
8	MeOCH <sub>2</sub> CH <sub>2</sub> N <sup>+</sup> Me <sub>3</sub> BF <sub>4</sub> <sup>-</sup> ·LiBF <sub>4</sub>	-61	-110(0.5);-78(2.1)	106(10.0)
9	Mixture 75% of 2 - 25% of 1	-74	-107(1)	83(7.0)
10	Mixture 50% of 2 - 50% of 8	-71	-133	83
11	Mixture 25% of 2 - 75% of 8	-65	-95(1)	89(8.4)
12 <sup>e</sup>	MeOCH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> BF <sub>4</sub> <sup>-</sup>	-115	-	-16(16.1)
13	MeOCH <sub>2</sub> N <sup>+</sup> EtMe <sub>2</sub> ·LiBF <sub>4</sub>	-	-85(0.4);-22(0.7)	90(4.2)
-	-	-	10(0.9);27(0.8)	-
14	MeOCH <sub>2</sub> N <sup>+</sup> Me <sub>3</sub> BF <sub>4</sub> <sup>-</sup>	-	-	46(12.6)
15	MeOCH <sub>2</sub> N <sup>+</sup> Me <sub>3</sub> ·LiBF <sub>4</sub>	-68	-18; 12(1.2);40(1.1)	66(1.9)
16	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> EtMe <sub>2</sub> BF <sub>4</sub> <sup>-</sup>	-	-68(0.7);38(1.7)	158(3.6)
17	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> N <sup>+</sup> EtMe <sub>2</sub> BF <sub>4</sub> <sup>-</sup> ·LiBF <sub>4</sub>	-	-139(1.5);-45(0.2);	165(8.2)
-	-	-	34(0.8);79(0.5)	-

a - degrees °C; b - glass transition temperature (vitrification by liquid N<sub>2</sub> quench except for No. 6 which vitrifies in DSC at 320°/min); c - enthalpies of transition and of melting in cal/g; d - this compound also shows a complex pattern of low-temperature phase transitions, very history-dependent; e - the cation of this salt is apparently reported here for the first time.

heating rates. The heats of transformation were determined using the Perkin-Elmer software on the data station, using indium as a reference. Melting points are believed correct to  $\pm 2^\circ\text{C}$ , and transition enthalpies to  $\pm 5\%$ .

#### *Electrical conductivity.*

The electrical conductivities were determined on samples which were crystallized in a conductivity cell the design of which has been described elsewhere<sup>11</sup>. The cell constant was 0.327; the distance between the platinized electrodes (0.5 cm) prevented trapping of air bubbles between them. The state of the sample could be observed periodically since the cell is of Pyrex glass. The conductance was measured using a GENRAD Model 1689 Digibridge, operating in the frequency range  $12 \cdot 10^5$  Hz. Some problems were encountered with crystal-electrode contact which could be partly lost after quick cooling, especially during the initial crystallization from the melt. For compound 2 (see Table 1), cooling from  $100^\circ$  melt to R.T. at  $15^\circ/\text{hr}$  yielded results reproducible to within 5% at R.T. on second use. At lower temperatures, the annealing effects were more pronounced and the conductivities drifted upward; e.g., after cooling to  $-24^\circ\text{C}$  the conductivity changed from  $0.77 \times 10^{-7}$  to  $1.15 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$  over a period of 10 hrs. Frequency dependence of conductivity was negligible at and above room temperature. Although this study is preliminary in nature we believe the conductivities of this salt to be correct to within 5%, which is satisfactory given the number of steps involved in the total synthetic-purification-measurement series.

Reproducibility of conductivity results was poorer for the other salts (e.g., for 4,  $\sigma$  drifted upward by 20% at R.T. over a month period) and the frequency dependence of conductivity was significant. Cole-Cole plots showed clearly the presence of extraneous effects (electrode contacts, grain boundaries).

## RESULTS

The double salts prepared as described above in most cases appeared as translucent masses which, however, were not as soft to mechanical probing as might have been expected from the magnitude of the thermal transitions reported below. After passage through the phase transitions at low temperatures, the translucence was lost, but could be regenerated by refusion and crystallization. Microscopic examination of a sample of 2 inside the transparent conductivity cell revealed that the stress caused by the shrinkage on slow cooling from the melt did not result in separation between the sample and either the electrodes or the glass walls of the cell, but rather in formation of what seem to be thin, elongated bubbles. Since gas bubbles were practically absent from the melt, their rounded contours seem to testify to relatively rapid crack healing and partial sintering along grain boundaries formed during freezing. This is precisely the behavior expected from a mass of plastic crystals, and it is also consistent with the positive drift of conductivity with time. A sample of the analogous perchlorate complex (compound 4) displayed a similar appearance. By contrast, a sample of 17 (in which the methoxyethyl group is replaced by the butyl group which is similar in size and shape but much more restricted in motion), shows a pattern of sharp, unhealed cracks and straight grain boundaries; it is also more hard and brittle and has a very low conductivity.

As seen in Table 1, there are significant differences in melting points between the tetrafluoroborates and iodides. Since the volume excluded by  $\text{BF}_4^-$  and  $\text{I}^-$  are only a little different, and since the packing in the salts must be determined primarily by the bulky cations, it would seem that the difference in melting points reflects differences in polarization energies rather than coulomb energies. The wealth of solid-solid phase transitions in the tetrafluoroborates and perchlorates, as opposed to the iodides, is probably related to the non-spherical symmetry of the  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  anions.

We note that only one case, that of polyethylene oxide + lithium iodide, has a superior conductivity. The activation energies are comparable, as are the electrochemical stabilities, so that the relative merits of the two lithium-conducting systems must be decided on other issues. In this respect the following advantages of the PLICFIC-type of solid electrolyte should be emphasized.

Because the anions are located on the points of a crystal lattice<sup>12</sup>, their diffusivity is necessarily small compared with that of the disordered  $\text{Li}^+$  species, so the transport number of  $\text{Li}^+$  should be close to unity. This compares favorably with the situation in the polymer electrolytes in which estimates of the transport numbers of the anions range between 0.1 and 0.6,<sup>3b</sup> but in no instance are zero. Finite transport numbers for the anions lead to a distinct decrease in electrochemical efficiency, and thus it is probable that the PLICFIC-type electrolyte is preferable in principle. We should, however, make the cautionary note that anion mobility has been observed in crystalline quaternary ammonium bromides<sup>13</sup>, though the conductivities remain some three orders of magnitude below the present values at the comparable temperatures. Also it seems unlikely that an asymmetric ion like  $\text{BF}_4^-$  could diffuse with the ease of a bromide anion.

The principal advantage of polymer-based systems is their ability to deform under mechanical stress, and thus to adjust to changes in electrode volume. Although the plasticity of the solid electrolytes we describe here has not been quantitatively evaluated at this time, the expectation is that in optimized cases, the ability to deform under stress will approach or exceed that of lithium sulfate in its FIC phase which is almost waxy, in its behavior. The rheological properties of  $\text{Li}_2\text{SO}_4$  have been studied using penetration viscometry techniques<sup>14</sup>, and these methods will be applied to the present systems in future work.

The question now becomes one of improving on the properties of the methoxy-ethyl dimethyl ethylam-

monium tetrafluoroborate based double salt 2 which was the first prepared in this study. We have sought to increase the solid-solid transition enthalpy, with the possibility of both thermodynamical and kinetic improvements in mind. Thermodynamically, a higher  $\Delta H_{tr}$  is likely to result in an increased entropic stabilization of the plastic phase, hence a higher melting point, thus widening the useful temperature range of the PLICFIC. Kinetically, one would expect the lower melting enthalpy to be accompanied by higher solid state plasticity and faster ion reorientation rates at ambient temperature, hence improved conductivity. To this end we have followed three lines of investigation, none of which have so far yielded the sought-after results.

(a) In the first place we have reduced the asymmetry of the head group by replacing the ethyl side chain by a third methyl in the hope of improving the rotational freedom of the cation, (to which it is reasonable to expect the rotational freedom of the anion to be related). This was done using two different tail groups, methoxy-methyl and the original methoxy-ethyl. The size-reduction of the organic ion by one or two  $\text{CH}_2$  groups was expected to raise the melting point. In all these cases, however and also for some mixtures of the compounds, the low-temperature transitions were smaller in magnitude and no significant gain in melting point was obtained. Lower melting enthalpies were obtained in two cases, 13 and 15, however, and these compounds merit further work.

15 in particular should be pursued since the entropy of fusion is characteristic of a true "plastic" crystal. The conductivity of a mixture of two compounds entry 11 in Table 1 was measured and found to be almost an order of magnitude lower than that of our best compound.

(b) As a second variation we retained the original head group but replaced the methoxyethyl tail group by an equally long alkane group (17 in Table 1). This also led to a decreased conductivity. It seems probable that the ether group plays a role in the easy migration of the  $\text{Li}^+$ , possibly by providing

a modified energy barrier between most favored  $\text{Li}^+$  sites.

(c) A third approach was to try to improve plasticity, and possibly to decrease activation energy for conduction, by replacing the  $\text{BF}_4^-$  ion with larger complex ions. To this end we prepared some of the tetrachlorogallates of the quaternary cations listed in Table 1 (preparation of the tetrachloroaluminates failed because of the high reactivity of  $\text{AlCl}_3$  towards the ether oxygen). We were encouraged to find some extremely soft plastic crystals in this group. Preparation of their complexes with  $\text{LiGaCl}_4$  or  $\text{LiAlCl}_4$  failed, however, because of incomplete dissolution of the lithium salts in the melt, and of considerable decomposition. Preliminary results seem to indicate that analogous silver-based compounds, with plastic characteristics, exist. This approach seems sound in principle and warrants further work.

Thus while the potential of the PLICFIC material is established by the data of Figure 2, it is not clear at this point how to proceed from the promising to the superior material. A possible synthetic improvement to this could be the replacement of the ether oxygen in the organic cation with sulfur, since thioethers are known to be much more resistant to Lewis acid attack than ethers<sup>15</sup> and are also more conformationally labile<sup>16</sup>. While sulfur would probably be less effective than oxygen in solubilizing  $\text{Li}^+$ , it may be very effective with softer cations ( $\text{Ag}^+$ ,  $\text{Cu}^+$ ). We should emphasize that it is not yet established that the conductance mechanism involves the coupling of cation motion to the anion rotations (paddle wheel mechanism) as suggested for  $\text{Li}_2\text{SO}_4$ .<sup>4,6</sup> One of the features of the latter material which indicates the paddle wheel mechanism is that not only the  $\text{Li}^+$  but other cations, including divalent cations which are doped into the host structures, exhibit unusual mobilities. We have yet to test the present PLICFICs for such interesting and diagnostic behavior. Solid state  $^6\text{Li}$  and  $^{11}\text{B}$  NMR studies on compound 2, which suggest that the anions are rotating rapidly above 60 - 70°C and that the  $\text{Li}^+$  cations are mobile will be reported in a separate paper<sup>17</sup>.

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C. A. Angell  
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Purdue University  
Department of Chemistry  
West Lafayette, IN 47907  
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## ALL-HALIDE SUPERIONIC GLASSES

Changle Liu, H.G.K. Sundar and C. A. Angell  
Department of Chemistry  
Purdue University  
West Lafayette, Indiana 47907

To date all the highest-conducting  $\text{Ag}^+$  and alkali cation glasses have involved admixture of a halide, usually the iodide, with some oxyanion salt of the same cation. In this paper we report cases where the oxyanion can be omitted. Instead, a second cation ( $\text{Cs}^+$  or  $\text{Rb}^+$ ) is introduced to provide, together with a mixture of anions, the immobile quasi-lattice through which the mobile cations,  $\text{Ag}^+$  or  $\text{Cu}^+$ , can migrate. The materials are evidently vitreous state analogs of the well-known superionic crystals  $\text{CsAg}_4\text{I}_5$  and  $\text{RbCu}_4\text{I}_5$ . In these new systems, conductivities at  $25^\circ\text{C}$  can reach record values. Glass transition temperatures, however, are lower than for oxyanion-containing glasses of the same conductivity. Since they contain only heavy monovalent ions, the far IR transparency of the new glasses is unprecedented. The characteristics of stress relaxation for both electrical and mechanical stresses are studied and are compared with those of the oxyanion + halide glasses. The all-halide glasses show less exponential relaxation (broader distributions of relaxation times) despite equivalence of all  $\text{Ag}^+$ . They nevertheless show smaller deviations from the Arrhenius law in their temperature dependences.

### 1. INTRODUCTION

This laboratory recently reported the existence and characteristics of fast ion conducting glasses in which no oxyanions or other complex species are present.<sup>1</sup> The glasses contained only monovalent cations and anions, the anions being chloride and iodide and the cations being silver and cesium. Although these glasses are generally characterized by low glass transition temperatures, they are of interest (a) because of their simple constitution, (b) because those richest in silver salts give the highest electrical conductivity so far measured at room temperature, and (c) because, in contrast to previous  $\text{Ag}$  oxysalt +  $\text{Ag}$  halide systems, it is reasonable to suppose all the  $\text{Ag}^+$  ions present to be equally mobile. Comparison of properties with those of the oxysalt-halide glasses may therefore throw light on those features of the

behavior which are related to mixed mobility properties.

In the present article we extend the study of glasses of all-halide type to the  $\text{Cu}^+$  analogs, and examine the a.c. conductivity as well as the d.c. conductivity characteristics. We will also introduce comparisons with mechanical relaxation studies, and with the known properties of oxyanion-based silver halide glasses.

### 2. EXPERIMENTAL

Chemicals used were all high purity substances obtained from Merck, and Alfa, and Chemical Cos. The lowest purity level was 99.8% for  $\text{CuCl}$ . Glassforming regions in the various tertiary and

quaternary systems, e.g., AgCl-AgI-CsCl, CuCl-CuI-RbCl-RbCl, and CuCl-CuI-RbCl-KCl, were identified by quenching weighed mixtures melted in Pyrex glass tubes at 500 - 600°C, between cold metal plates. In favorable cases thick pellets of glass could be formed by natural cooling on the metal plate.

Discs formed by quenching were coated on each side with a standard area of silver paint, and their electrical conductivities were determined using a standard two terminal arrangement. The temperature range -170°C to room temperature, was covered by allowing slow temperature rise from an initial liquid nitrogen environment in a Dewar flask, readings over the frequency range 12-100,000 Hz being taken automatically by a computer controlled GENRAD digibridge model 1689 in the manner described by Martin and Angell.<sup>2</sup> For the highest temperature ranges the conductivities were too high for the (low cell constant) disc arrangement to be satisfactory. For these cases linear strip samples were cut from the discs, and copper foil electrodes pressed in contact at the ends as indicated in the inset to Fig. 4. d.c. conductivities were determined using the complex impedance plots shown in Fig. 1. The diagram shows the extreme temperature ranges of data obtained with linear strip samples.

For the disc configuration samples, in which fringing effects are absent, the real and imaginary parts of the complex impedance contain information on the kinetics of electrical relaxation in the bulk vitreous material. The relaxation of electrical stress in vitreous media is not exponential, and the departure from exponentiality is currently generating considerable interest among chemical physicists.<sup>3</sup> Since the present system shows greater departures from exponential relaxation than ever previously observed for ionic conduction processes we present some of the data in form suitable for further analysis in Fig. 2. Fig. 2 shows the real and imaginary parts of the complex electrical modulus,  $M^* = M' + iM''$ ,  $= 1/\epsilon^*$ . We discuss these data further below.

To obtain some information on the relaxation of

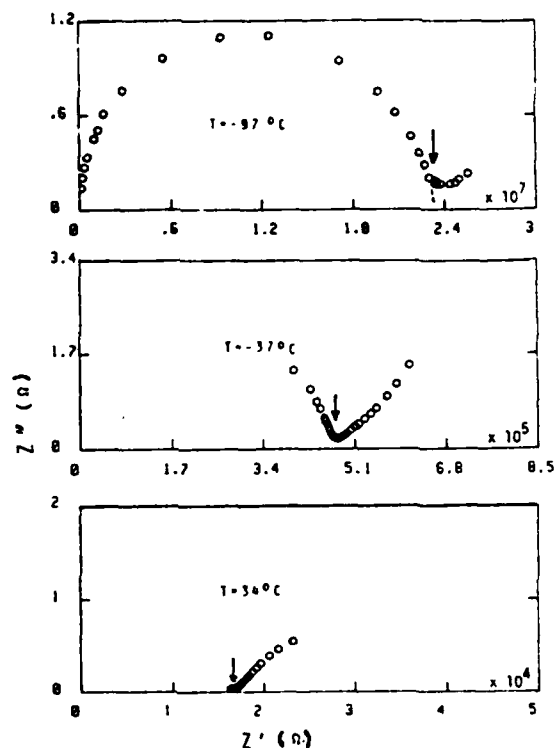


Fig. 1. Complex impedance plots for linear strip sample of AgI-AgCl-CsCl glass at various temperatures showing definition of  $\sigma_{dc}$ .

mechanical stresses at frequencies overlapping those of the electrical measurements, linear strip samples cut from the initial discs were mounted in a stirrup configuration illustrated in Fig. 7 below and subjected to sinusoidal flexural deformations using a Toyo Instruments Rheovibron. The instrument reads out the ratio of the imaginary to real parts of the complex tensile modulus  $E^*$  as the loss tangent,  $\tan \delta$ . This can be determined continuously during slow temperature rise from -160°C. Results for the present and previous<sup>4,5</sup> systems show that  $\tan \delta$  for fast-ion conducting glasses rises to a maximum value at some temperature determined by the chemical constitution of the glass, before going off scale as  $T$  approaches  $T_g$ .

To determine the attempt frequency for the fundamental barrier crossing step involved in the

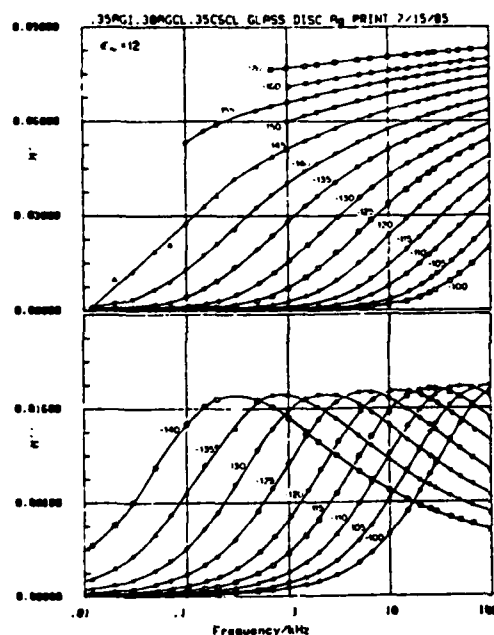


Fig. 2. Real and imaginary parts of the complex electrical modulus 0.35AgI, 0.30AgCl, 0.35CsCl glass obtained using disc sample.

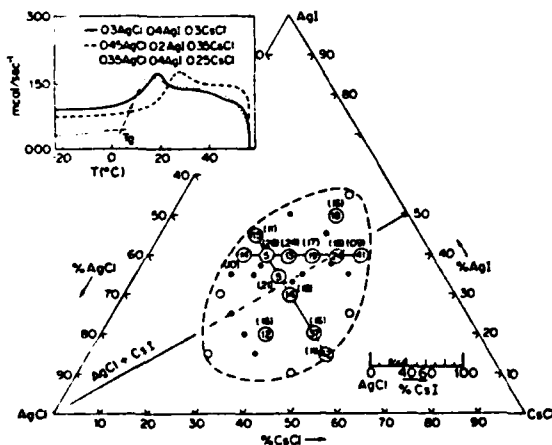


Fig. 3(a). Glassforming composition region and glass transition temperatures in AgCl-AgI-CsCl ternary systems. DSC scans are shown above for some cases.

relaxation processes, and to evaluate the IR transparency, infrared spectra were obtained using a Perkin Elmer Model 567 for the range  $> 200 \text{ cm}^{-1}$ . Far IR spectra have been obtained on AgI - AgPO<sub>3</sub> and CuI - CuPO<sub>3</sub> glasses, but not, so far, on the all-halide glasses due to difficulties associated with the low  $T_g$  values.

### 3. RESULTS AND DISCUSSION

The glassforming regions for several Ag<sup>+</sup> and Cu<sup>+</sup>-based ternary and quaternary systems are shown in Fig. 3. Glasses high in CuCl have particularly low glass temperatures, which may be raised by PbCl<sub>2</sub> additions. The  $T_g$  values for glasses rich in RbCl or CsCl are quite high, comparable with those observed in mixed Ca<sup>2+</sup>/K<sup>+</sup> nitrate glasses<sup>6</sup>. Note that a line of glasses across the middle of the ternary system AgCl-AgI-CsCl corresponds to compositions in the simple binary system AgCl-CsI. A number of compositions that we have studied in detail correspond to compositions in this binary system and will be referred to as such in the text and figures.

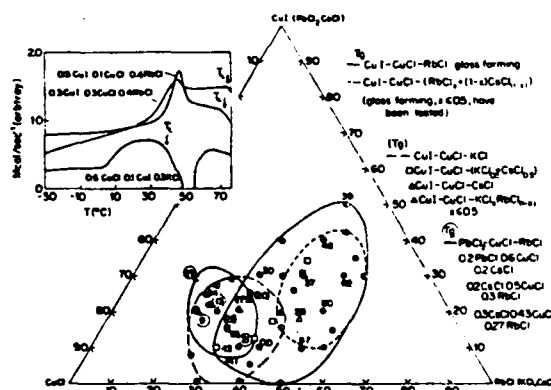


Fig. 3(b). Glassforming composition regions and glass transition temperatures for four types of CuCl-based halide glass systems. For key to  $T_g$  identification, see legend. Half-filled symbols indicate mixed glass and crystal from quench.

The d.c. conductivities for various compositions in the  $\text{Ag}^+$ -containing and  $\text{Cu}^+$ -containing glasses of Fig. 3 have been extracted from Figure 1 type data representations and are shown in Figs. 4 and 5 respectively. Not surprisingly, the highest conductivities are obtained with the highest  $\text{Ag}^+$  and  $\text{Cu}^+$  contents. For the silver systems, the trend with composition at constant  $\text{AgCl}$ , or constant  $\text{AgI}$ , contents respectively, are shown in the inset.

The conductivities for the silver halides are extremely high. Comparisons with the best silver ion-conducting glasses known from previous work<sup>7,8</sup> are made in the inset to Fig. 4. Unfortunately, these remarkable conductivities are obtained at the expense of rather low glass transition temperatures. Data on systems in which the all-halide glasses are incorporated progressively in oxyanion matrices (by analogy with the previously studied  $\text{AgI-AgPO}_3$ , and  $\text{AgI-AgBO}_2$  systems) will be described in separate publications.

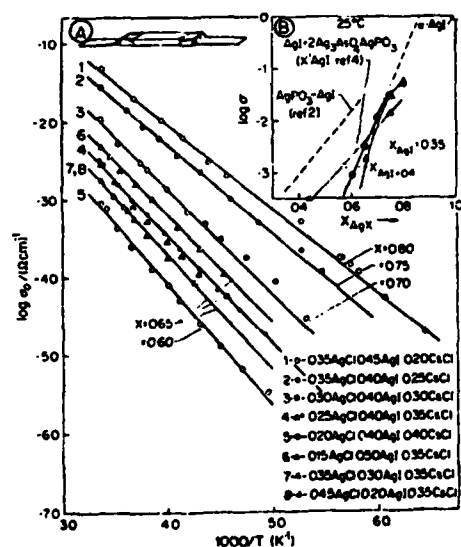


Fig. 4. Arrhenius plot of conductivity for AgCl - AgI - CsCl glasses. Insert: composition dependence of ambient temperature conductivity.

The conductivities of the  $\text{Cu}^+$  halide glasses at low temperatures are considerably greater than those of the best  $\text{Cu}^+$ -conducting glasses previously reported<sup>10</sup> ( $\text{CuI} + \text{CuPO}_3$ ). However, due to their low glass transition temperatures, the highest-conducting compositions cannot be studied at room temperature.

Fig. 5 contains, as the highest-conducting sample, an interesting material obtained by controlled crystallization of an initially glassy material containing 14%  $\text{PbCl}_2$ . The glass itself has a low glass transition temperature,  $10^\circ\text{C}$ , and crystallization occurs over a period of 2 hrs at room temperature. The material produced, however, retains its transparent character though the conductivity increases considerably as a consequence of the crystallization. This material also retains considerable mechanical strength and is immune to attack by atmospheric moisture. It is potentially a very interesting material for both conductivity and infrared transmission purposes.

Turning now to the spectroscopic characteristics of the electrical response we note that in Fig. 2 the full width at half-height, FWHH, is much greater than

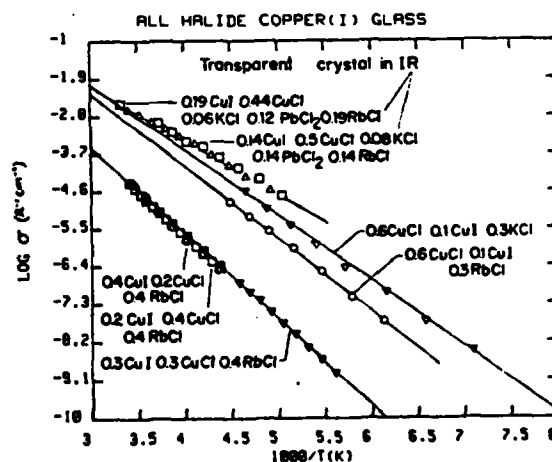


Fig. 5. Arrhenius plot of CuCl - based glasses. Note that the highest - conducting case is a devitrified metastable crystal containing  $\text{PbCl}_2$ .

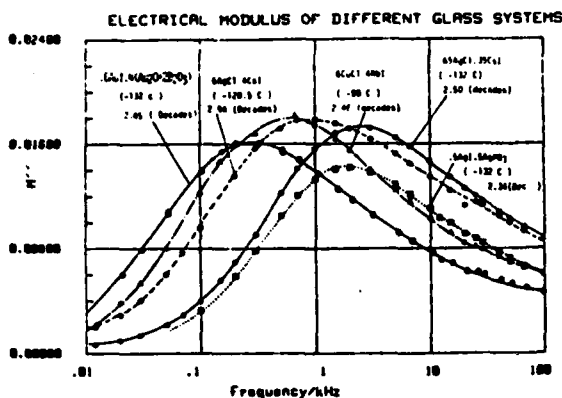


Fig. 6. Comparison of electrical loss spectra for various AgCl-CsI, AgI-Ag oxyanion glasses and CuCl-CuI-RbCl. FWHHs marked on diagram.

for Debye relaxation, as is almost always the case for ionic conduction in glasses. The FWHHs we observe, however, are exceptional. We compare  $M''$  spectra for several glasses of the present and previous study in Fig. 6 and note the existence of FWHHs generally greater than two decades and approaching three decades in the case of 0.6AgCl 0.4CsI. This implies a value of the exponent  $\beta$  in the Kohlrausch-Williams-Watts relaxation expression<sup>11,12</sup>

$$\phi(t) = e^{-(t/\tau)^\beta} \quad (1)$$

of 0.36, the smallest yet recorded for electrical relaxation. We find also a weak tendency to broaden as temperature decreases for a given glass, the opposite behavior from that found in silicate glasses.<sup>13</sup> The breadth of the spectra in these exceptionally high conductivity glasses continues a trend noted in a recent study by Martin and Angell<sup>2</sup> which correlates decreasing  $\beta$  with increasing conductivity at fixed temperature.

It is of interest to compare the electrical relaxation with that observed for mechanical stresses. Note that where an electrical stress (instantaneous field created by placing opposite charges on either side of a sample) will be completely dissipated by movement of

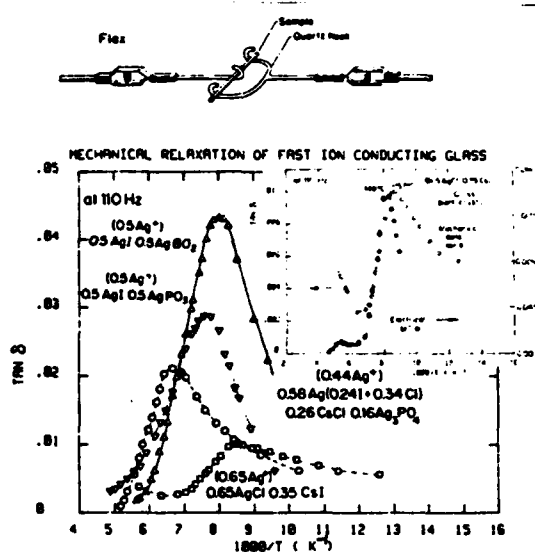


Fig. 7. Tan  $\delta$  plots at 110 Hz vs  $1/T$  (to give frequency spectrum form). Insert: Comparison of electrical and mechanical loss scans at 100 Hz.

ions across the sample, a mechanical stress will not. Rather a deformation to a limiting value characteristic of the stressed state will occur. Since the mechanical measurements are limited in their frequency range we present the observations as scans in temperature at fixed frequency. They are shown in Fig. 7 plotted vs  $1/T$  so that the same form as in Fig. 3 will be obtained. (This is rigorous if the FWHH is constant with  $T$ , and the Arrhenius Law is obeyed, as is approximately true in the present case). We include data for other  $\text{Ag}^+$ -containing systems with different oxyanions, for comparison. Data for  $\text{Cu}^+$ -containing oxyanion glasses showing similar features are published elsewhere.<sup>5</sup>

It is notable that the all-halide glasses, besides having their loss peaks at the lowest temperatures (expected from their higher conductivities), have spectra very much broadened at low temperatures. This indicates the presence of a high density of fast-relaxing modes, and is the opposite of what might have been expected of a system in which all silver ions

may be presumed equivalent. Certainly this finding must raise much doubt about the possibility of attributing spectral width in oxysalt-halide glasses to populations of different intrinsic mobility<sup>14</sup>. Because of the equivalence of form, a FWHH in  $1/T$  can be converted to an approximate FWHH in frequency. The value implied is an extraordinary 8 decades. A comparison with the electrical relaxation is made in the insert to Fig. 7 where electrical modulus  $M''$  data are shown scanned in temperatures at fixed frequency. The mechanical spectrum is strikingly broader at lower temperatures (high frequency) implying mechanically excitable modes which have no dipole moment associated with them. It is probable that this sample has suffered partial crystallisation during preparation. Therefore some spectral distortion could be due to nucleus-matrix surface modes and further study will be needed to decide whether the exceptional behavior observed is intrinsic to the glass. The width of the more crystallisation - resistant mixed system  $\text{AgPO}_3 + (\text{halide glass})$  seen in Fig. 6, suggests that it is. In this case, unusual behavior may be expected in the cryogenic range where anomalous specific heat and thermal conductivity properties are generally found.

Some interesting features are observed in the electrical modulus behavior in partially crystallised samples. Fig. 7 (insert) shows the presence of a bump at low  $1/T$  corresponding to a second and slower electrical relaxation such as may be seen in electrolyte solutions<sup>15</sup>. This phenomenon will be analysed in more detail in a separate publication<sup>9</sup>.

Finally, we combine all the relaxation time data available for these glasses into a single Arrhenius plot (Fig. 8) to show how both mechanical and electrical relaxations have a common origin in the quasi-lattice vibrational modes seen in the Far IR. In the case of the all-halide glass the absorption centered at  $\approx 100 \text{ cm}^{-1}$  (which causes the IR cut-off for thick sections at  $\approx 300 \text{ cm}^{-1}$  shown in the insert) is the only IR absorption, in contrast to the case of the oxyanion - containing glasses. An example of extended range mechanical relaxation data covering 10 orders of magnitude (for an  $\text{AgI} \cdot [\text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3]$  glass) is included for com-

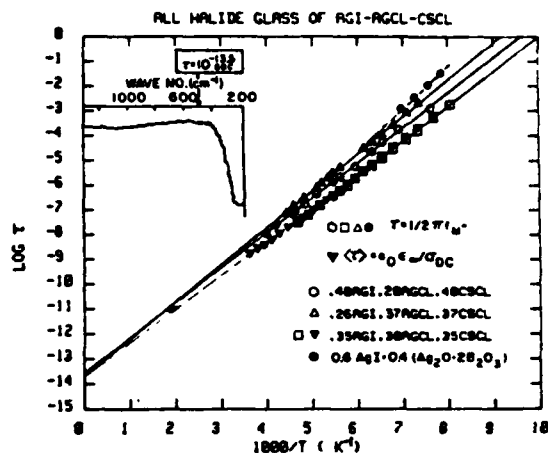


Fig. 8. Arrhenius plot of electrical and mechanical relaxation times, showing extrapolation to infra-red absorption frequency. Included are mechanical data for an  $\text{AgI} \cdot \text{Ag}_2\text{O} \cdot 2\text{B}_2\text{O}_3$  glass.

parison (see Borgesson and Torell, this proceedings). Although the  $M''$  spectra are the broadest yet observed, the relaxation times show very little of the deviation from Arrhenius behavior seen frequently for the iodide - oxyanion glasses<sup>16</sup>.

An advantage of the all-halide systems is that they are non-corrosive and low-melting hence lend themselves to precision measurements in the mobile liquid state. We are currently extending the study of the dynamics of these systems to temperatures where the limiting high conductivity will be closely approached in order to complete the "map" presented in Fig. 8 and, in addition, to show how the decoupling of electrical and primary structural relaxation occurs as  $T_g$  is approached from the liquid state.

#### ACKNOWLEDGEMENTS

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